Structures of decagonal quasicrystals and crystalline approximants, studied by highresolution electron microscopy(高分解能電子顕微鏡による正10角形準結晶と近似結晶の構造に関する研究)

著者	孫 威
号	1600
発行年	1993
URL	http://hdl.handle.net/10097/6873

氏名	Sun 孫 Wei 威
授与学位	博士（工学）
学位授与年月日	平成6年3月25日
学位授与の根拠法規	学位規則第5条第1項
研究科，専攻の名称	東北大学大学院工学研究科 （博士課程）材料物性学専攻
学位論文題目	Structures of decagonal quasicrystals and crystalline approximants, studied by high-resolution electron microscopy（高分解能電子顕微鏡による正10角形準結晶と近似結晶の構造に関する研究）
指導教官	東北大学教授 平賀 賢二
論文審査委員	東北大学教授 平賀 賢二　東北大学教授 早稲田嘉夫 東北大学教授 井上 明久　東北大学助教授 進藤 大輔

論文内容要旨

Chapter 1 Introduction

Quasicrystals are a new class of ordered atomic structures which exhibit long-range quasiperiodic translational order and long-range orientational order with disallowed crystallographic symmetry. Quasicrystals can be mainly divided into two basic categories, i. e., the tree-dimensional icosahedral quasicrystal (I-phase) and the two-dimensional decagonal quasicrystal (D-phase). The decagonal quasicrystal has two-dimensional quasiperiodicity and periodicity along its tenfold symmetry axis. The existence of decagonal quasicrysrals with different periods, such as 0.4nm, 1.2nm and 1.6nm, has been reported. It is considered that decagonal quasicrystals with 0.4nm, 1.2nm and 1.6nm periods correspond to 2-layer, 6-layer and 8-layer structures, respectively. It seems that there is a fundamental repeat unit of 0.4 nm. However, it is not yet clear what are the origin and structure of this unit.

To understand the real structures of the decagonal quasicrystals, one has to resolve what kinds of structural units form local atomic arrangements and how these units arrange to form long-range quasiperiodic structures. Unfortunately, little has been done to understand how

the basic structure units are made up and how they construct decagonal quasicrystal structure so far.

High-resolution electron microscopy is a powerful tool for investigating real structures of quasicrystals from the micron scale to the atomic scale. In particular, the observed images of decagonal quasicristals, taken with the incident beam parallel to the tenfold axis, directly reveal quasiperiodic arrangements in two-dimension. In the present work, the decagonal quasicrystals with various periods of 0.4nm, 1.2nm and 1.6nm and their structurally related crystalline approximants were studied by means of high-resolution electron microscopy. Our purpose is to reveal the following items :

(1) local atomic arrangements of the structural units and long-range arrangements of the units in the decagonal quasicrystals.

(2) structures of crystalline approximants, and their structural relationships with decagonal quasicrystals.

(3) the formation process of the Al-Pd-Mn decagnoal quasicrystal from the crystalline approximant and from the I-phase.

(4) structural changes of the Al-Cu-Co decagonal quasicrystals by heat treatments.

Chapter 2 Experimental procedure

In this chapter, the experimental procedures for sample preparation, X-ray diffraction, EDX analysis were described, and the experimental conditions for high-resoluction electron microscopy, the parameters used for image calculations and a method used for analysis of high-resolution images of the decagonal quasicrystals were presented.

Chapter 3 Decagonal quasicrystal and crystalline approximants with 1.2nm periodicity

In this chapter, the Al-Pd-Mn D-phase with 1.2 nm periodicity was studied in detail. The formation region, structural characteristics and growth modes of the D-phase have been clarified. In addition, the structure of an approximant found in Al-Pd-Cr system was also investigated.

The Al-Pd-Mn D-phase was found to be formed by annealing at 800℃ in a wide composition range. A single D-phase zone was found to exist at 800℃ around the composition of $Al_{70}Pd_{13}Mn_{17}$. It has been clarified by high-resolution electron microscopy that the structure of the Al-Pd-Mn D-phase is constructed by a space-filling tiling of atom clusters with decagonal symmetry (D-units), star-shaped pentagons (P-units) and squashed hexagons (H-units) (see Fig. 1). From high-resolution structure images, the similarity of the local structure to the Al_3Mn crystalline phase and computer simulation, reasonable atomic arrangements in the D-,

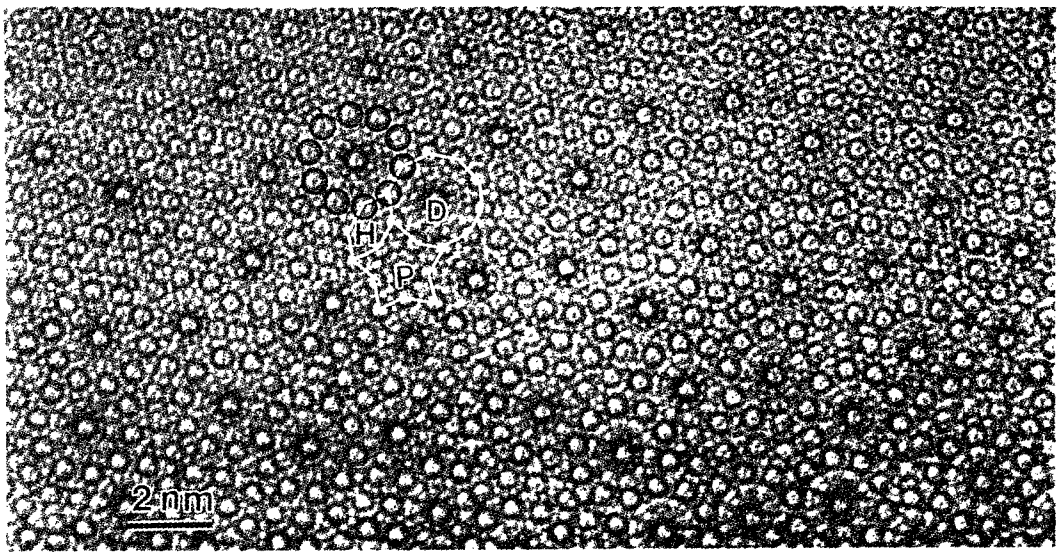


Fig. 1 High-resolution image of the Al-Pd-Mn decagonal quasicrystal taken with the incident beam parallel to the tenfold symmetry axis.

P-and H-units have been proposed. The fact that configurations periodic tilings of thses units can form various crystalline approximants has been clearly revealed.

A new orthorhombic approximant consisting of P-and H-units was found in an $Al_{72}Pd_{18}Cr_{10}$ alloy annealed at 80℃, and its atomic structure model was proposed. In the as-castd $Al_{72}Pd_{18}Cr_{10}$ alloy, however, a structure constructed by random arrangement of the P- and H-units was found.

Two kinds of growth processes of the Al-Pd-Mn D-phase have been revealed. The first of these is that the D-phase grows from a crystalline approximant π-phase by the segregation of decagonal atom clusters. The decagonal atom clusters rearrange, connect with difinite linkages and establish a long-range correlation by annealing at 800℃ for a significant long time. In the second, the D-phase grows from an I-phase with epitaxial crystallographic relationships between them. It has been revealed that the growth interface of the D-phase to the I-phase consists of coherent interfacial facets and some ledges. The interfacial facets are along the tenfold plane of the D-phase which is parallel to the fivefold plane of the matrix I-phase. Growth of the D-phase in the I-phase proceeds through lateral movement of the interfacial ledges on the tenfold plane.

Chapter 4 Decagonal quasicrystal and crystalline approximants with 0.4 nm periodicity

In Chapter 4, the structural characteristics of Al-Ni-Co and Al-Cu-Co D-phases with 0.4

nm periodicity were revealed. A highly ordered D-phase showing long-range correlations was found to be formed in the $Al_{70}Ni_{15}Co_{15}$ and $Al_{65}Cu_{20}Co_{15}$ alloys quenched from 800℃, and its structure was characterized by a pentagonal tiling of atom clusters, which could be interpreted as the Penrose tiling containing some random phason strains. On the other hand, it was found that the D-phases quenched from 800° in the $Al_{70}Ni_{15}Co_{15}$ and $Al_{65}Cu_{20}Co_{15}$ alloys underwent a structural change by annealing at low temperatures (about 600℃). The structures of the low temperature phases are characterized by rhombic tilings of the same atom clusters as those in the D-phases at high temperatures. An atomic arrangement of the atom cluster in the Al-Ni-Co D-phase has been proposed, which can interpret the observed high-resolution images well.

In addition, various crystalline approximants have been found in the Al-Co-Pd system. An orthorhombic approximant with parameters of $a = 2.0$nm, $b = 0.4$nm and $c = 2.35$nm, constructed by atom clusters of Penrose skinny rhombus, was found in the as-casted $Al_{70}Pd_{10}Co_{20}$ alloy. A monoclinic approximant ($a=2.0$nm, $b=0.41$nm, $c=3.0$nm and $\beta=108°$) was found in an as-casted $Al_{76}Co_{20}Pd_4$ alloy. The structure of the monoclinic approximant is characterized by the giant pentagonal cluster, which is τ^2 time larger than the pentagonal atomic column in the Al_3Mn crystalline approximant.

Charpter 5 Decagonal quasicrystal and crystalline approximants with 1.6nm periodicity

In Chapter 5, the structural characeristics of the D-phase with 1.6nm periodicity and the related crystalline approximants have been revealed.

The D-phase with 1.6 nm periodicity was found to be formed as a metastable phase in an $Al_{75}Pd_{20}Mn_5$ alloy by rapid solidification, and as a stable phase in an as-casted $Al_{76}Co_{20}Pd_4$alloy. It is clearly revealed that the structures of these two D-phases can be interpreted as a quasiperiodic tilling formed with a definite vertix sharing linkage of the pentagonal atom columns. In the as-cated and annealed $Al_{75}Pd_{20}Mn_5$ and $Al_{76}Co_{20}Pd_4$ alloys, various crystalline approximants were found. Their structures can be interpreted as periodic tilings formed with the same linkage of the pentagonal atom columns as that in the D-phases.

Chapter 6 Summary

In this chapter, the results obtained in the present study are summarized. The structural characteristics of the D-phases and the crystalline approximants with various periods of 0.4 nm, 1.2 nm and 1.6 nm were discussed.

The D-phases and crystalline approximants with various periods of 0.4 nm, 1.2 nm and 1.6 nm contain atom columns as the most fundamental structure units (Fig. 2). The various

periods of the D-phases are determined by the periods of the corresponding pentagonal atom columns. The structural characteristics of the D-phases and their approximants can be systematically understood by two-dimensional arrangements of the pentagons surrounding the pentagonal atom columns. The edge lenght of each pentagon is $a_0 = 0.475$ nm, which is an importance distance to determine not only the characreristic linkage distances in the tilings of the D-phases, but also the lattice parameters of crystalline approximants.

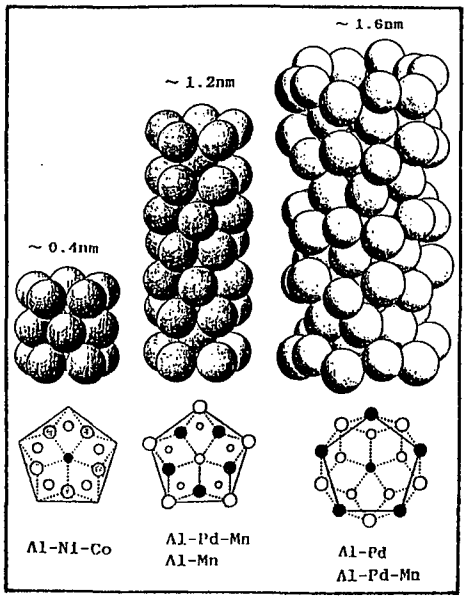


Fig. 2 The most fundamental structure units for constructing the decagonal quasicrystals with various periods and the related crystalline approximant.

As can be seen in Table 1, the small pentagons which represent pentagonal atom columns are connected by an edge-sharing linkage in the D-phases with 0.4 nm and 1.2 nm periodicity, and by a vertex-sharing linkage in the D-phase with 1.6 nm periodicity. The definite linkages of the pentagons form various polygons as structural units. The most important one of them is the decagonal atom cluster (D) for the D-phases with 0.4 nm and 1.2 nm periodicity. Main structures of the D-phases with 0.4 nm and 1.2 nm periodicity are formed by quasiperiodic arrangements of the decagonal atom clusters, which are joined with definite linkage manners (see Table 1), and the gaps in the arrangements of the atom clusters are filled up with other polygons formed with pentagons. Decagonal atom clusters (D_L) also appear in the D-phase with 1.6 nm periodicity, but their long-range arrangements can not be seen. Instead, the pentagonal atom columns play the role of the decagonal atom clusters to make up the main structure of the D-phase with 1.6 nm periodicity.

The quasiperiodic arrangements of the structural units formed with the atom columns with the definite linkages construct various tilings, which determine the long-range structural characteristics of the D-phases. On the other hand, the periodic arrangements of these structural units with the same linkages form various structures of approximants.

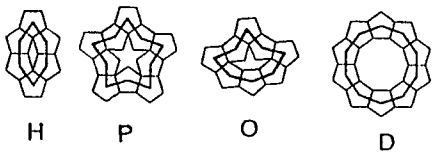
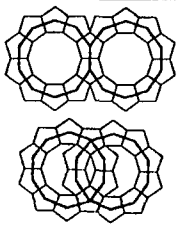
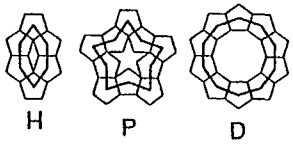
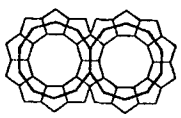
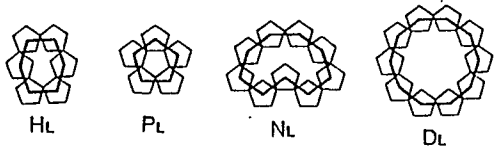
Periodicity	Structural units formed with atom columns (pentagons)	Linkage manners
0.4 nm		
1.2 nm		
1.6 nm		

Table 1 Typical structural units (polygons) formed with pentagonal atom columns and the difinite linkage manners.

審 査 結 果 の 要 旨

結晶に存在し得ない対称性を持ちながらシャープな回折パターンをつくる準結晶は，結晶および非晶質と並ぶ新しい構造群として認知されてきた。本研究は，10回対称軸に沿って0.4nm，1.2nm，1.6nm 周期をとる 3 種類の正10角形準結晶と準結晶の周辺に現れる結晶相（近似結晶）の構造を，主に高分解能電子顕微鏡を用いて研究した成果をまとめたもので，全編 6 章よりなる。

第 1 章は序論であり，本研究の背景と目的を述べている。

第 2 章では，試料製作および実験法について述べている。

第 3 章では，1.2nm 周期をとる Al-Pd-Mn 正 10角形準結晶の安定領域を決定し，その構造が 5 角形原子カラムの決まった結合で構成される 6 角形，星型 5 角形，正 10 角形原子クラスターの 2 次元配列で理解できることを明らかにし，その原子配列モデルを提出している。さらに，4 種類の近似結晶相の構造が同じ原子クラスターの周期配列で理解できること示している。また，結晶相から正 10 角形原子クラスターの発生および再配列によって，高い規則性の正 10 角形準結晶が形成されることを見いだしている。

第 4 章では，0.4nm 周期の $Al_{70}Ni_{15}Co_{15}$，$Al_{65}Cu_{15}Co_{20}$ 合金の正 10 角形準結晶を対象に，それらの構造が，正 10 角形原子クラスターを構造単位として，それらの決まった結合できた 2 次元配列として理解できることを見いだし，その原子クラスターの原子配列モデルを提出している。また，これらの合金において，約800℃以上の高温で高い規則性の5角形タイリングの準結晶が形成され，低温でひし形タイリングに変態することを見いだしている。

第 5 章では，1.6nm 周期の正 10 角形準結晶と近似結晶について，液体急冷した $Al_{75}Pd_{20}Mn_5$ 合金で形成された準安定な正 10 角形準結晶および $Al_{76}Co_{20}Pd_4$ 合金で見いだされた安定な正 10 角形準結晶の構造が，5 角形原子カラムの点共有の配列で理解できることを見いだしている。また，通常の溶解法で作られた $Al_{75}Pd_{20}Mn_5$ 合金で種々の近似結晶を見いだすと共に，それらの構造が同じ原子カラムの点共有の配列で理解できることを示している。

第 6 章では，成果を総括すると共に，3 種類の周期の異なる正 10 角形準結晶および近似結晶の構造の関連性を議論し，それらが原子カラムの 2 次元配列で系統的に理解できることを示している。

以上要するに本論文は，正 10 角形準結晶とそれに関連した近似結晶の構造を明らかにすると共に，それらの構造が基本の構造単位（原子カラム）の 2 次元配列で系統的に理解できることを示したもので，材料物性学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。